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A Rheokinetic Study of Bulk Free Radical Polymerization Performed with a Helical Barrel Rheometer

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The Trommsdorff effect is a non-linear autoacceleration phenomenon in bulk free radical polymerizations. It is undesired in processes of industrial scale, as it causes hot spots and erratic behavior. In this paper a rheokinetic investigation of the Trommsdorff effect is performed with a helical barrel rheometer. This rheometer can be considered a small-scale model of large reactors, particularly extruders. The rheokinetic measurements show that the Trommsdorff effect can be reduced when the polymerization is performed at a high rotational velocity of the screw. This confirms a previous study performed with a cone and plate rheometer and is encouraging with a view to designing better-controlled bulk free radical polymerization processes of industrial scale.

INTRODUCTION

According to the general theory (1, 2), the rate of a bulk free radical polymerization can be expressed as

$$R = -\frac{d[M]}{dt} = \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} k_p[I]^{\frac{1}{2}}[M] \qquad (1)$$

The negative sign is added in order to have an intrinsically positive expression of the rate of polymerization. f is the initiator efficiency, k_i, k_p and k_t are the rate constants of the initiation, propagation and termination reactions respectively, and [I] and [M] are the concentrations of the initiator and of the monomer.

Bulk free radical polymerizations are often characterized by an autoacceleration phenomenon called the Trommsdorff or gel effect (3). The Trommsdorff effect usually takes place at intermediate or high degrees of conversion and is caused by diffusion limitations that hinder the mobility of macromolecules. Therewith the rate constant of the termination step k_t decreases, since the termination reaction can take place only when two growing radicalic macromolecules collide with each other. In contrast, the diffusion of small monomer molecules, and therefore the rate constant of the propagation step k_p, are barely affected.

As Eq 1 shows, a decrease of k_t results in an increase of the rate of polymerization.

The Trommsdorff effect takes place also when the polymerization is performed in controlled isothermal conditions and should not be confused with the "Arrhenius" autoacceleration that would take place in non-controlled conditions, because of the increase of temperature connected with the heat released by the polymerization.

The Trommsdorff effect is highly undesired in industrial processes. It leads to thermal runaway and formation of hot spots, which causes erratic and unpredictable behavior and may even lead to the explosion of the reactor (4, 5).

The scientific literature concerning the Trommsdorff effect has been reviewed recently (3). Most of the research efforts so far have been directed at gaining a deeper understanding of the Trommsdorff effect on the molecular scale. This is of primary importance if the problems caused by the Trommsdorff effect are to be solved. However, a similar effort is missing when it concerns methods to reduce or eliminate the Trommsdorff effect. Although the Trommsdorff effect could successfully be reduced in a couple of specific cases

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(6, 7), control of this phenomenon still remains, generally speaking, an unsolved problem.

In a previous paper (8) we performed a rheokinetic study of the bulk free radical polymerization of styrene and n-butylmethacrylate with a cone and plate rheometer.

Rheokinetics is a relatively new field of research. It can be defined as the rheological study of reacting polymeric systems (9, 10). Its main objectives are:

- to model and predict the increase of viscosity during a polymerization reaction and to understand how it is influenced by the experimental conditions (temperature, catalyst or initiator concentration, shear rate).
- to study the kinetics of the polymerization by means of rheological measurements performed during the polymerization

We demonstrated that the Trommsdorff effect can be reduced or even eliminated when the polymerization is performed at high shear rate. In this paper, we report and discuss the experimental results of a similar rheokinetic study performed with a helical barrel rheometer.

This rheometer is geometrically similar to a single-screw extruder. It therefore permits measurement of the viscosity in a configuration similar to those encountered in several industrial reactors. It can also be used for on-line measurements of viscosity in industrial processes (11, 12).

MATERIALS

Solutions of glucose syrup and water were used to test the reliability of viscosity measurements performed with the helical barrel rheometer and for the calibration.

Styrene and n-butylmethacrylate were purchased from Sigma Aldrich and used without further purification. The bulk free radical polymerization was initiated by thermal decomposition of a peroxide, Trigonox 42S (Akzo Nobel).

METHODS. THE HELICAL BARREL RHEOMETER

The helical barrel rheometer is essentially a small single-screw extruder. It can be used as a batch reactor (closed die) to measure the increase in viscosity during polymerization. As the term "helical barrel rheometer" suggests, the thread is mounted on the barrel and not on the rotating element. If the thread were mounted on the rotating element, as in ordinary extruders, it would pass along the pressure sensors, and this would result in oscillations and inaccuracy of the measurement of the pressure drop, and therefore of the viscosity (11).

The viscous flow in the axial direction in the helical channel of a conventional extruder is usually characterized by a volumetric drag flow Q_d and a pressure flow Q_p.

$$Q_d = \frac{\pi DWhN\cos\theta}{2} \tag{2}$$

$$Q_p = \frac{Wh^3\,\Delta P\sin\theta}{12\eta L} \tag{3}$$

where N is the screw rotational speed, D is the screw diameter, W is the width of the channel, θ is the screw helix angle (i.e. the angle of the flights with the axis of the screw), h is the channel depth, ΔP is the pressure difference measured over the length L and η is the viscosity.

The volumetric drag flow is directed towards the die of the extruder, the pressure flow in the opposite direction.

At closed discharge, the drag flow and the pressure flow must be equal and opposite, since the overall flow must be equal to zero.

$$Q_d = Q_p \tag{4}$$

Substituting Eqs 2 and 3 into Eq 4, we obtain

$$\eta = \frac{\Delta Ph^2}{6\,N\pi^2D^2} \tag{5}$$

if we set L, the distance over which ΔP is measured, equal to $\pi D\tan(\theta)$, the axial width of one flight.

Therefore measuring the pressure difference with two pressure sensors, it is possible to determine the increase of viscosity during the polymerization.

The helical barrel rheometer used in this study was constructed at the University of Groningen and is shown in Figs. 1 and 2. During the experiments the metering section of the helical barrel rheometer was positioned in a steel housing (not shown in the figures) that was electrically heated. The heaters were connected to a temperature controller (Plasticorder PL 2000-6, Brabender, Duisburg, Germany). The temperature was stable during the experiments and only small deviations from the set point ($\pm$ 1°C) were noticed.

The helical barrel rheometer was preheated to the desired temperature and the monomer and the initiator were mixed at the desired concentration just before beginning the experiment.

The measurements were stopped when the pressure inside the helical barrel rheometer reached 30 bar, in order not to damage the pressure sensors and the rheometer itself. Occasionally, samples were thermally quenched at the end of the experiments and tested by nuclear magnetic resonance. This revealed that conversion was almost complete.

To our knowledge, only Todd et al. (11) successfully performed viscosity measurements of polymer melts with a helical barrel rheometer, but the device has not yet been used for rheokinetic investigations.

The major qualitative difference between the cone and plate rheometer and the helical barrel rheometer regards the shear flow profile to which the polymerizing liquid is subjected. For the cone and plate rheometer,

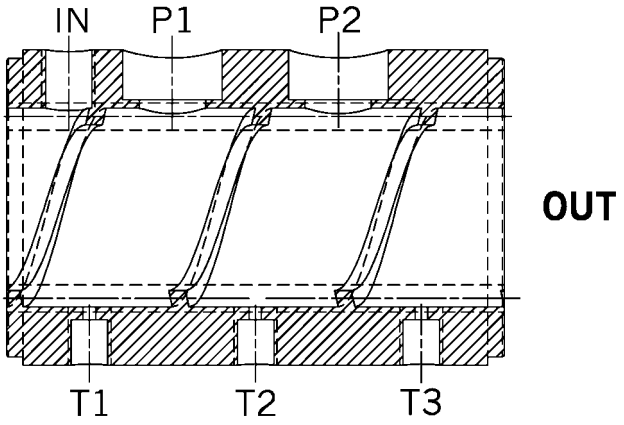

Fig. 1. The Helical Barrel Rheometer. A section view of the measuring part of the HBR is here reported. The monomer-initiator solution is fed through the "IN" until it fills up the gap completely. The HBR is heated electrically and the heating system is connected to a control system. P1 and P2 are the positions of the pressure sensors. T1, T2 and T3 are the positions of three thermocouples used to check that the temperature of the sample is uniform across the whole rheometer. After the experiment the polymer is removed through the "OUT".

the shear rate is the same everywhere in the sample, whereas the helical barrel rheometer is characterized by a very complicated profile of the shear rate.

Because of the uniform shear rate, the cone and plate rheometer is ideal for investigating the influence of shear rate on the rheological properties of polymeric systems. However, the shear flow profile that it generates is very different from those occurring in industrial applications.

In contrast, the helical barrel rheometer induces a very complicated shear flow profile, more like those occurring in industrial applications, especially in reactive extrusion.

Determining the shear flow profile and the average shear rate in the helical barrel rheometer is a complex mathematical problem that will not be dealt with in this paper in detail. In first approximation, we can assume that the channel between the helical barrel and

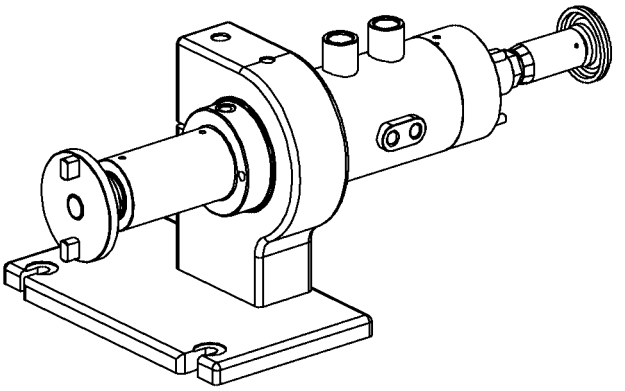

Fig. 2. The Helical Barrel Rheometer as it looks from the outside.

the screw is equivalent to the gap between two parallel infinite plates. One plate is fixed and the other plate moves horizontally with velocity equal to πDN and a pressure drop contrary to the direction of the movement of the plate is applied (see Fig. 3).

It can be demonstrated that the velocity profile for a Newtonian fluid is parabolic and that the average shear rate $\dot{\gamma}_{av}$ is given by:

$$\dot{\gamma}_{av} = \frac{5}{3}\frac{\pi ND}{h} \tag{6}$$

The average shear rate is therefore proportional to the velocity of the horizontal plate, or, in other words, to the rotational speed of the screw.

Todd et al. (11) showed that also for non-Newtonian fluids a similar relationship is valid for the helical barrel rheometer. The coefficient in the right-hand side of Eq 6 is different. In particular, this coefficient is a function of the power law index of the non-Newtonian fluid.

In this paper we report the data obtained performing the experiments at a value of N included between 2 rpm and 60 rpm. According to Eq 6, this corresponds for the helical barrel rheometer used in this investigation to values of the average shear rate included between 5 and 150 s^{-1}. These values are of the

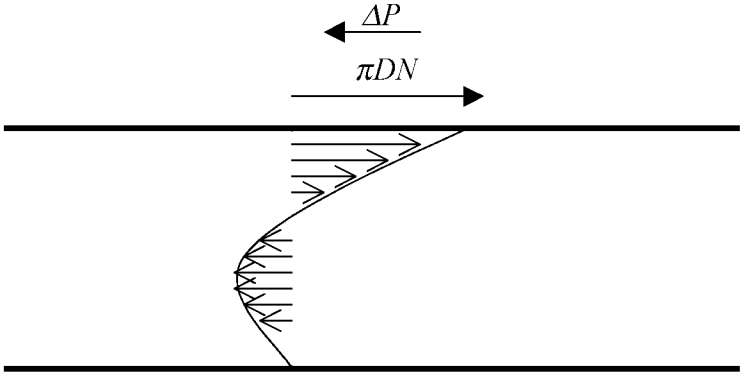

Fig. 3. The approximated velocity profile in the helical barrel rheometer.

same order of magnitude as those concerning our previous rheokinentic study performed with a cone and plate rheometer (8).

In conclusion, it can be stated that the helical barrel rheometer, in analogy with the cone and plate rheometer, permits experiments at different average shear rate, varying the velocity of the rotating element.

We can argue that the helical barrel rheometer represents a scale-up of experiments performed previously with a cone and plate rheometer. In fact, the volume of the polymerizing sample in the helical barrel rheometer (about 30 ml) is an order of magnitude larger than in a cone and plate rheometer (about 1 ml) but still very small if compared to those of industrial reactors of extruders. However, the qualitative difference between the two geometrical configurations is significant.

Therefore the helical barrel rheometer is an ideal tool for a rheokinetic study of the Trommsdorff effect in conditions similar to those encountered in industrial polymer processing, particularly reactive extrusion.

Our major interest was to check if a high shear rate can reduce the extent of the Trommsdorff effect also when performing the polymerization in a reactor more like those used in industrial applications. Therefore, the dimensions of the helical barrel rheometer were chosen to allow measurements of high viscosities, corresponding to high conversions. The helical barrel rheometer used in this experimental study is not reliable at the beginning of the polymerization, where, anyway, the Trommsdorff effect is not expected to occur.

RESULTS

The reliability of our self-constructed helical barrel rheometer was tested performing viscosity measurements with water solutions of glucose syrup and comparing the results with those obtained with the cone and plate rheometer used in our previous investigation. These solutions are Newtonian and therefore allow comparing viscosity measurements performed in different devices characterized by different flow regimes. The results are reported in Table 1 and show a good agreement between the cone and plate rheometer and the helical barrel rheometer.

Table 1. Viscosity Data Obtained With a Cone and Plate Rheometer and With the HBR for Two Water Solutions of Glucose Syrup.

Helical Barrel Rheometer (Pa.s)	Cone and Plate Rheometer (Pa.s)
0.21	0.19
0.39	0.41

The increase of viscosity during bulk free radical polymerization was measured in different experimental conditions. Whatever the temperature, the initiator concentration or the monomer used, the trend of the viscosity versus time curves was qualitative the same. One typical example is shown in Fig. 4.

The data could be well fitted by two power law curves, fitted to the upper and lower sections of the data.

$$\eta = at^b \tag{7}$$

The border between the two curves was chosen so as to maximize the values of the regression parameter R^2. In all cases the first power law exponent was lower than the second.

This result is in good agreement with the literature concerning the rheokinetics of bulk free radical polymerization (2, 8, 13, and 14). In fact, the viscosity

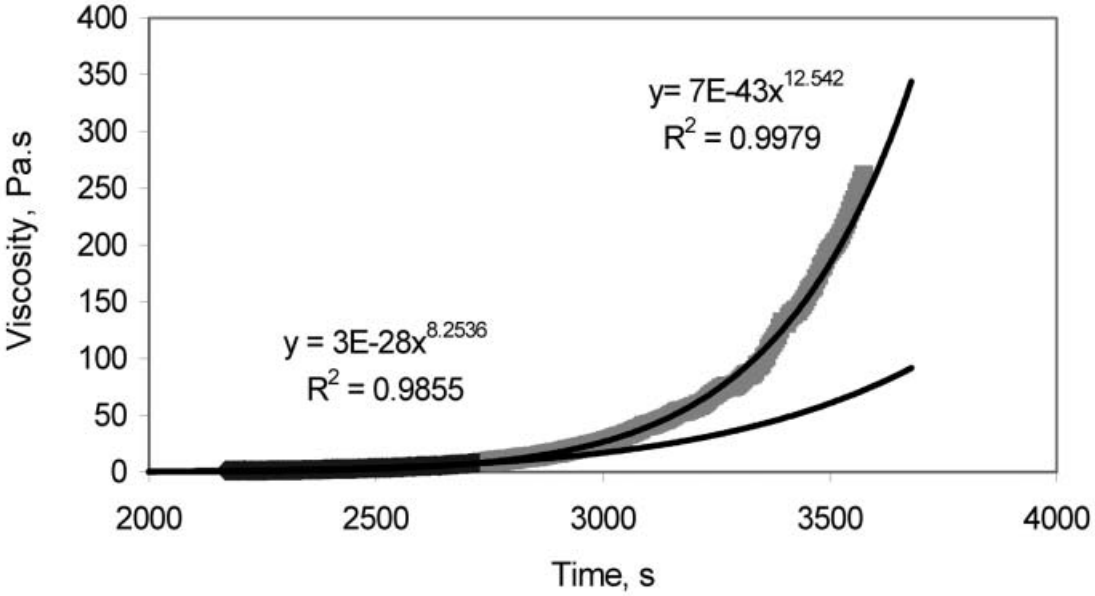

Fig. 4. The double power law trend for the increase of viscosity during the polymerization of n-butylmethacrylate at 100°C. N = 10 rot/min. $[I]_0$ = 1% v/v. For the first 2000 seconds of the experiments the viscosity is too low for the sensitivity of the Helical Barrel Rheometer.

increase can be divided in three regions, characterized by different values of b:

1) $b \approx 1$ at the very beginning, where the degree of conversion is very low and there are no entanglements between macromolecules.
2) $5 < b < 7$ at higher conversions, but while the polymerization proceeds at a constant rate and no diffusion limitation (Trommsdorff effect) occurs.
3) $b \gg 7$ at high degrees of conversion, where the Trommsdorff effect takes place.

Our data refer to the last two regions. As already mentioned before, our helical barrel rheometer could not give reliable values of the viscosity in the early stage of the polymerization.

The difference between the two values of b obtained by fitting the viscosity measurements can be considered as a measure of the Trommsdorff effect (8).

Experiments were performed at different rotational velocities (i.e. different average shear rate), but otherwise the same experimental conditions, in order to verify the influence of shear rate on the Trommsdorff effect.

The data regarding n-butylmethacrylate are shown in Figs. 5 and 6. They show clearly that the Trommsdorff effect can be reduced performing the bulk free radical polymerization at a higher rotational velocity of the rotating element or, in other words, at a higher average shear rate. This phenomenon can be ascribed to the fact that shear induces order into the system, reducing the degree of entanglement and orientating the macromolecules. This results in a decrease of the diffusion limitation to the movement of the growing macromolecules, which is the root cause of the Trommsdorff effect.

The observed reduction of the Trommsdorff effect cannot be ascribed to shear-thinning. In fact, if that were the explanation, the power law exponents would not level off as reported but would continue to decrease with an increasing rotational velocity of the screw, i.e. with an increasing average shear rate.

In the case of the experiments performed with styrene, a remarkable extension of the initial lag time of the polymerization was noticed, which affected the values of the power law exponents. They are in the range 20–40. These values are not in agreement with the results obtained with the cone and plate rheometer (8), where no conspicuous difference could be observed between styrene and n-butylmethacrylate. These exponents are also not in agreement with other rheokinetic studies published by other authors (2, 13, and 14).

A complication of the experiments with styrene was the formation of bubbles inside the helical barrel rheometer. Their formation can be ascribed to the fact that the boiling temperature of styrene (145°C) is too close to the temperatures at which the experiments were performed (110–120°C).

However, these bubbles could be removed slowly during the experiments. Nevertheless, during the initial phase of the experiments, the helical barrel rheometer was partially empty and the monomer-initiator solution had to be added gradually as long as bubbles were removed.

Since a large amount of monomer-initiator concentration had to be fed during the experiments, we can argue that the real initiation lag time must be shorter than the one resulting from the experiments. If initiation lag times similar to the ones obtained with n-butylmethacrylate are assumed, the data reported in Fig. 7 are obtained.

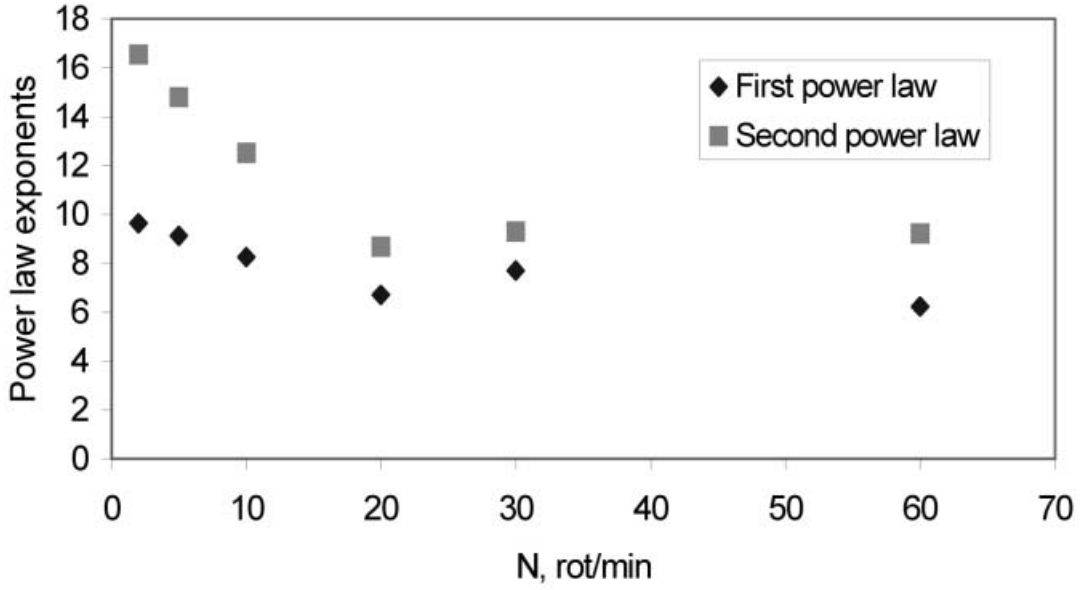

Fig. 5. The power law exponents for the polymerization of n-butylmethacrylate at different rotational speed of the screw. T = 100°C. $[I]_0$ = 1% v/v.

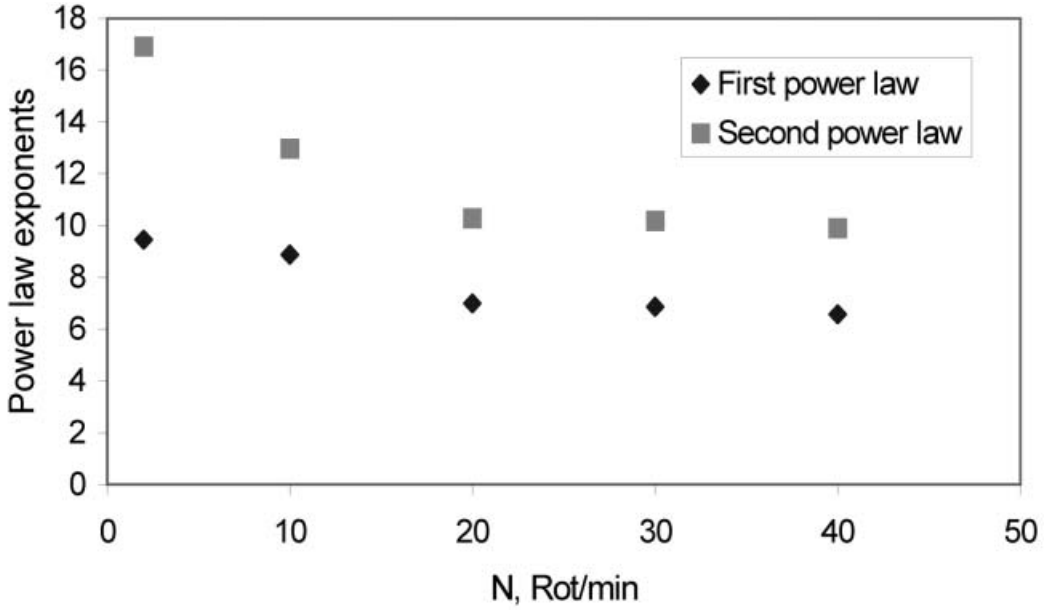

Fig. 6. The power law exponents for the polymerization of n-butylmethacrylate at different rotational speed of the screw. T = 110°C. $[I]_0$ = 0.33% v/v.

Although this procedure is not rigorous, the choice of the modified values of the lag times being to some extent arbitrary, Fig. 7 indicates that also for the bulk free radical polymerization of styrene the Trommsdorff effect can be reduced performing the polymerization at high rotational speed of the rotating element.

However, the evaporation of the monomer and the formation of bubbles inside the gap between the barrel and the rotating element are experimental evidence interesting in itself. In fact, they can explain the very high residence time required in the reactive extrusion of styrene to obtain a desired conversion.

Unfortunately, it was not possible to remove and quench samples at the end of the experiments in order to perform analyses of the average molecular weight. This has been done in the case of experiments performed at different shear rate with a cone and plate rheometer. The data obtained by size exclusion

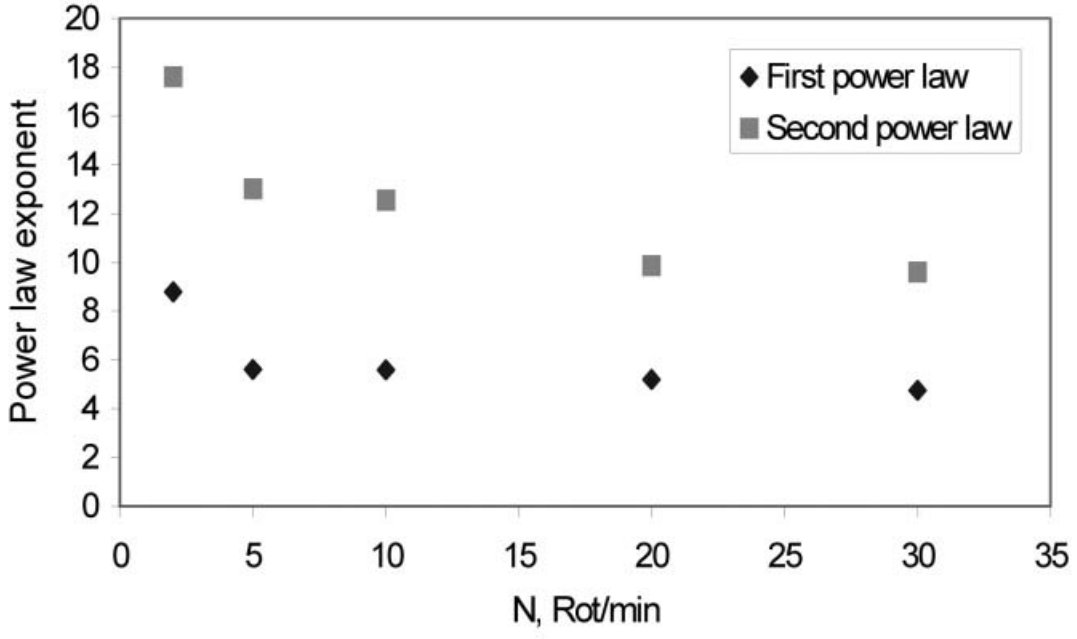

Fig. 7. The power law exponents for the polymerization of styrene at different rotational speed of the screw. T = 110°C. $[I]_0$ = 2.5% v/v.

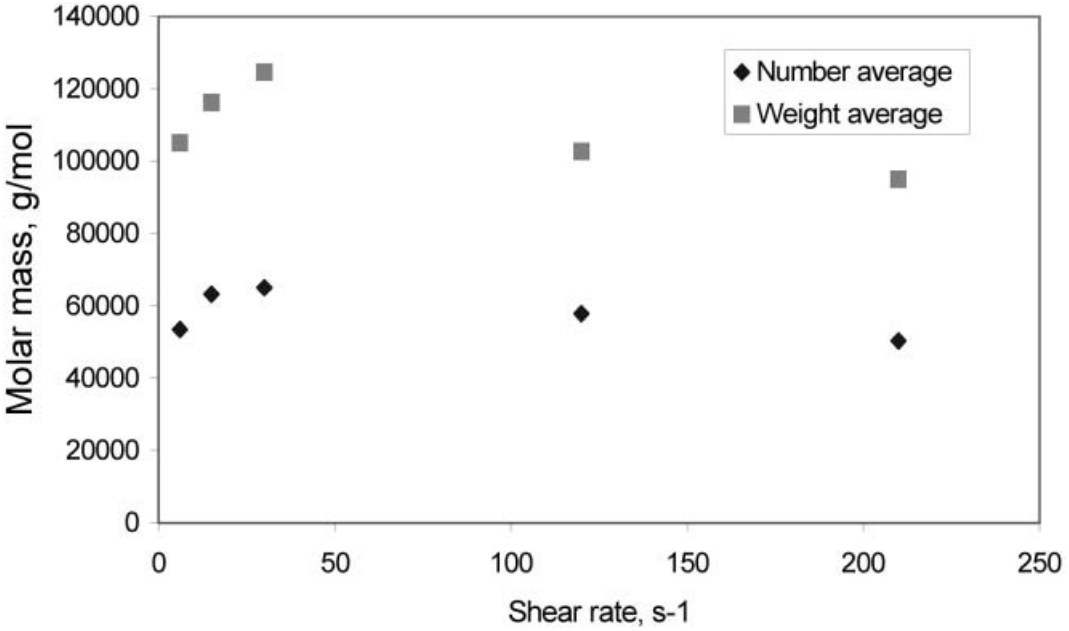

Fig. 8. The average molecular weight at the end of the polymerization of styrene at 116°C in cone and plate rheometer.

chromatography, reported in Fig. 8, show that the average molecular weight is not significantly influenced by shear. Therefore shear-induced degradation of the polymer can be ruled out as the underlying reason of the phenomena under investigation and, particularly, of the observed reduction of the Trommsdorff effect when the (average) shear rate is increased.

CONCLUSIONS

The helical barrel rheometer can be a useful tool for rheokinetic investigation. Its geometrical similarity with large-scale reactors, particularly extruders, makes it possible to perform a preliminary scale-up of results obtained with a classical cone and plate rheometer. Scale-up to industrial scale extruders on basis of data from the helical barrel rheometer is also far more reliable than based on data from cone-and-plate viscometry.

The results presented in this paper show that the Trommsdorff effect in bulk free radical polymerization of n-butylmethacrylate can be reduced performing the polymerization at a high rotational speed of the screw or, in other words, at a high average shear rate. Experiments performed with styrene were troubled by the evaporation of the monomer in their initial phase, but some considerations indicate that the same conclusion is valid also for styrene.

These results are in agreement with a previous study performed with a cone and plate rheometer and are encouraging in view of better-designed bulk free radical polymerization processes of industrial scale.

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